INDUSTRIAL ARCHAEOLOGICAL SITES AND ARCHITECTONIC REMAINS: THE PROBLEM OF CONSOLIDATION IN HUMID AREAS

Pittaluga D.[1], Fratini F.[2], Nielsen A.[3], Rescic S.[2]
[1] DSA Università di Genova, ISCUM, daniela.pittaluga@tiscalinet.it
[2] CNR-ICVBC, via Madonna del Piano10, Sesto Fiorentino (FI), rescic@icvbc.cnr.it, fratini@icvbc.cnr.it
[3]Nielsen Restauri, via della Maddalena 10, Genova, nielsenrestauri@tiscali.it

ABSTRACT

The article focuses on all those external areas that are to be maintained intact with respect to their amount of information, but which, due to their low resistance to atmospheric agents, require a superficial consolidation however made difficult by the presence of constant high humidity. The object of this research is a deposit of lime within the area of the "Fornace Bianchi", a site of industrial archaeology in Cogoleto (GE) (XIXth century). Three suitable inorganic consolidating products have been tested, ammonium phosphate, ammonium oxalate, nano-lime. These products, due to their inorganic nature, display high affinity and compatibility with the material object of the intervention compared to the normally used organic products. The reaction can take place even in damp conditions. Together with these products also nano-silica has been tested as comparison.

The ammonium phosphate has been recently studied and in contact with $CaCO_3$ develops its strengthening action through the formation of calcium phosphate hydrate (hydroxyapatite). The ammonium oxalate, used as "passivation" of carbonate stone surfaces for several decades, develops its action forming calcium oxalate.

Key-words: archaeological sites, consolidation, humidity, remains, ammonium phosphates

Introduction

The problem of preserving architectural structures often in ruins and constituted by low consistency materials, is common to many archaeological sites and is very timely. A possible action could be a protection from erosion due to rain flow with kind of shelters but this solution often leads to unacceptable aesthetic damages, not to mention the possibility of influencing the microclimate triggering unexpected degradation phenomena. Two emblematic cases can be mentioned:

- the UNESCO World Heritage Site of Lalibela in Ethiopia, where most of the rock hewn churches realised in a bank of low coherence volcanic rock, in 2008 were "protected" from the rain with huge shelters structures. The consequence is that religious buildings that were to remain hidden and suddenly appear to the pilgrims, now manifest their presence from a great distance;
- the Greek theatre of Eraclea Minoa in Sicily, where the seats of the *cavea* made of a soft marly limestone, in the sixties were protected from rain with perspex sheets put very close to them, causing a greenhouse effect which favoured a strong biological grow. The proposed solution was a rigid steel structure with plastic laminates which now cover with a strong visual impact the whole *cavea*.

The other solution is the use of suitable consolidating products capable to give cohesion to very low coherence materials. The case of the "Fornace Bianchi" in Cogoleto, near Genoa is presented, which includes three lime kilns and related structures. It was in function from mid-XIXth century to the fifties of the XXth century. Abandoned, was recovered by a restoration between 2008 and 2011 [1, 2].

The magnesian limestone outcropping in this zone was widely known and exploited since the Middle Ages for its quality. In the XVIIIth century thirteen different groups of working furnaces are documented and furnaces and quarry fronts characterized the landscape of Cogoleto for a long time. At present only few remain of this activity are still standing (Fig.1a) and the municipality intends to preserve them in the best way. The kiln area under study is of particular interest for several reasons:

- most of the structures now visible was buried until November 2010 due to a landslide following the abandonment of the furnace and the subsequent use of the area as a rubbish dump. Particularly, most of the existing ground floor and part of the first floor were not visible. Consequently, these masonries, within the past 60 years, suffered very different situations: first exposed to atmospheric agents, then "protected" in the burial ground and then again exposed to atmospheric agents;
- the materials used in the construction are traditional lime mortars, bricks, dolomite stones and big serpentinite pebbles. The masonries are partly mixed masonry (stone-brick) summarily covered by a lime plaster and partly of brick still covered by a lime plaster. Particularly interesting is a semi-coherent heap of lime (Fig.1b), evidence of the past production activity, which contains under burnt dolomite stone fragment, lime fragments and coal. This deposit, so important in

this industrial site area, is exposed to atmospheric agent and, due to its low consistenc, risks to be completely lost;

- most of the structures is constantly moist.

(a)

(b)

Figure 1. The remains of "Fornace Bianchi"(a) and the semi-coherent heap of lime (b)

As solution to pursue the preservation of this deposit, the experimentation of consolidating treatments with inorganic products compatible with the nature of the material to consolidate and capable to exert their action also in high humidity conditions, was performed. This action was decided in common agreement among the municipality of Cogoleto, the DSA (Department of Architectural Science-University of Genoa) and CNR ICVBC.

Treatments tests

The products

The products were selected according to the current ideas of conservation that advocate the use of eco-friendly and compatible products. That means products which are not harmful to humans or for the environment and that at the meantime are compatible with the material to be preserved, in our case the lime. Due to the inorganic nature of the lime, the products we have tested are inorganic, ensuring good compatibility (compositional, physical and mechanical). Both new generation products such as nano-lime and di-ammonium hydrogen phosphate and a traditional product as ammonium oxalate have been considered [3-5]. For comparison, also nano-silica was tested although being a substance that in humid areas cannot exert a good consolidating action [5].

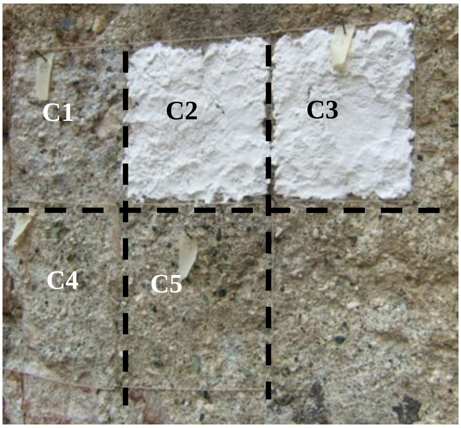
The treated materials

As stated in the introduction, the purpose of this research is to stabilize/consolidate the heap of lime, evidence of the production activity of the kiln. This heap has, however, extremely heterogeneous characteristics which made it impossible to select homogeneous areas in order to assess the effectiveness of different treatments. It was therefore decided to take, as testing areas, two plastered surfaces adjacent to the lime heap. The first one covers a mixed masonry made of bricks and serpentinite pebbles and it is located in front of the discharge mouth of the oldest kiln (area A), the second one covers a brick masonry and is located in the deposit of cocciopesto (area B). The study of the mineralogical composition of the two plasters showed that the former consists of a hydraulic lime mortar with a serpentinite aggregate while the second is formed by a mortar with a binder of magnesian calcite and serpentinite aggregate.

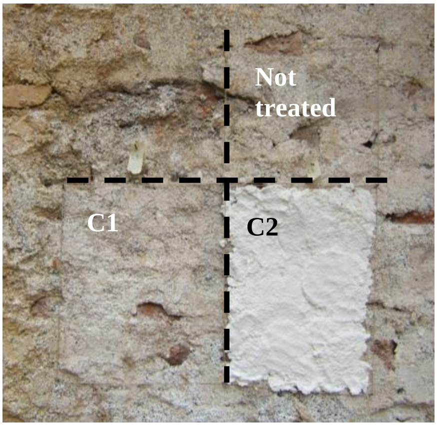
Methods of treatment

In A zone, the following products have been applied (Fig 2a):

- Syton X 30 (Kremer Pigments): nano-silica in aqueous solution applied with a brush until rejection, without dilution (30% w/w) (area A-C1);
- ammonium oxalate monohydrate (Sigma Aldrich pure reagent) in aqueous solution applied with cellulose pulp (5% w/w) (area A-C2);
- di-ammonium hydrogen phosphate (Sigma Aldrich pure reagent) in aqueous solution applied with cellulose pulp (10% w/w) (area A-C3);
- Nanorestore (CTS restoration): nano-lime made of nanoparticles of calcium hydroxide in isopropyl alcohol applied with a brush without dilution (area A-C4);
- untreated reference-area (area A-C5).



(a)



(b)

Figure 2. Area A made of hydraulic lime mortar (a) and area B made of magnesian lime mortar (b).

In B zone, the available surface was not sufficient to perform all the treatments. Therefore we have chosen the di-ammonium hydrogen phosphate (expected to perform good consolidating effectiveness-C2) and the nano-silica (C1), which in general has good performance. These products were applied according to the concentrations and described for A zone (Fig.2b).

Methods

The following tests have been applied on site in order to assess the performances of the consolidating products:

-colorimetric tests through a Minolta Chromameter CR200, with flash light C [6-8]. The co-ordinates L*(lightness), a*(green-red axis), b**(blue-yellow axis) have been determined on the not treated and treated area. The values were calculated as mean of 10 determinations for each area;

-drilling resistance test performed with the Drilling Resistance Measurement System (DRMS) [9-10]. The drilling resistance is correlated with the mechanical 'cohesion' of the masonry material. The values were calculated as mean of 3 tests for each treatment. The resistance tests were carried out using the drill bits for concrete and stone (Fischer 5mm diameter) selected from those having very close values of penetration resistance on ceramic reference material (ARS reference artificial stone) (maximum difference 0.5 -1 N). The operating conditions that are suitable on mortars are the following: of rotation speed of the tip 100rpm, forward speed of the tip 40mm/min, depth of the hole 10mm;

-water absorption tests performed trough the contact sponge method [11]. The values were calculated as mean of 3 tests for each treatment;

-compositional tests: for treatments such as ammonium oxalate and di-ammonium hydrogen phosphate tests of X-ray diffraction were carried out to determine the new formation phases due to the consolidation treatment.

Results

Colour measurements

In order to comment the data of the colour measurements, two key factors that may have influenced the measurements should be taken into account: the moisture content and the roughness of the surface. In particular, the B area is in permanent moisture due to the fact that is sited in a underground confined environment with the absence of air currents. The presence of moisture significantly affects the L* parameter, associated to brightness, with generally lower values in more humid areas, but it affects also the other colour coordinates (a*, b*) increasing the chromatic saturation (the so-called wet effect). The roughness of the surface generally increases the L* is parameter. Should also be noted that the slight colour unevenness of the surfaces due to the heterogeneous nature of the mortars, determines a dispersion of the values of the three colour coordinates (Tab.1).

In Table 2 the variations of the colorimetric coordinates (ΔL*, Δa*, Δb*) and the value of ΔE* (whose limit [= 5] indicates the colour changes detectable by the human eye) for the A and B areas are reported.

Table 1. Chromatic coordinates for the not treated A and B zones[+].

Area	L*	a*	b*
A	58.54±5.45	1.51±0.30	11.32±1.70
B	75.48±4.64	2.14±1.00	11.52±2.93

[+]mean values determined on 10 measurements

Table 2. Variation of the chromatic coordinates and ΔE* parameter for A and B areas.

Area	Treatement	ΔL*	Δa*	Δb*	ΔE*
A	Nano-lime	1.76	-0.36	-1.20	2.16
	Nano-silica	1.97	-0.62	-3.86	4.38
	Ammoium oxalate monohydrate	1.86	-0.46	-1.33	2.33
	Di-ammonium hydrogen phosphate	0.91	-0.19	-1.61	1.86
B	Nano-silica	-0.62	0.03	-1.11	1.27
	Di-ammonium hydrogen phosphate	-5.53	-0.51	-3.15	6.38

Δ= treated-not treated

In the area A a tendency to an increase in brightness (bleaching) and a shift to shades of blue and green can be observed. In particular it seems that the area treated with nano-silica changes significantly with ΔE* values around 4 and a significant contribution of the variation due to the b* coordinate.
With regard to the area B, a significant colour variation due to the treatment with di-ammonium hydrogen phosphate (ΔE* ~ 6) can be observed, with a significant contribution of L* (darkening) and b* (blueness). As regards the L* parameter, its variation may be due in part to the moisture of the surface.

Drilling resistance test

As for the colour test, we have to consider that the unevenness of the surface due to the presence of the aggregate and moreover a non-uniform thickness of the plaster, can make difficult the interpretation of the data. In Table 3 the average values of drilling resistance calculated over the entire range of drilling (0-10mm) are reported. As for area A, all the values show a quite high standard deviation (about 20% of the average value for almost all areas) but taking into account that the inhomogeneity is more or less similar within the various areas, it is possible to compare the treatments. On this basis, the data highlight that the di-ammonium hydrogen phosphate is the most effective product in consolidating the plaster, followed by ammonium oxalate, nano-silica and nano-lime.
The drilling resistance profiles make it possible a more accurate interpretation of the treatments effectiveness (Fig.3).

Table 3. Drilling resistance tests for A and B areas

Area	Treatment	Hole 1	Hole 2	Hole 3	Mean
		(N)			
A	Not treated	6.60	7.65	4.26	6.17±1.73
	Nano-lime	12.29	8.39	8.21	9.63±2.31
	Nano-silica	12.78	14.90	8.44	12.04±3.29
	Ammonium monohydrate oxalate	18.47	13.97	14.75	15.73±2.40
	Di-ammonium hydrogen phosphate	26.69	38.71	28.62	31.34±6.45
B	Not treated	11.08	14.13	14.36	13.19±1.83
	Nano-silica	3.44	6.71	8.39	6.18±2.52
	Di-ammonium hydrogen phosphate	20.69	13.28	16.65	16.87±3.71

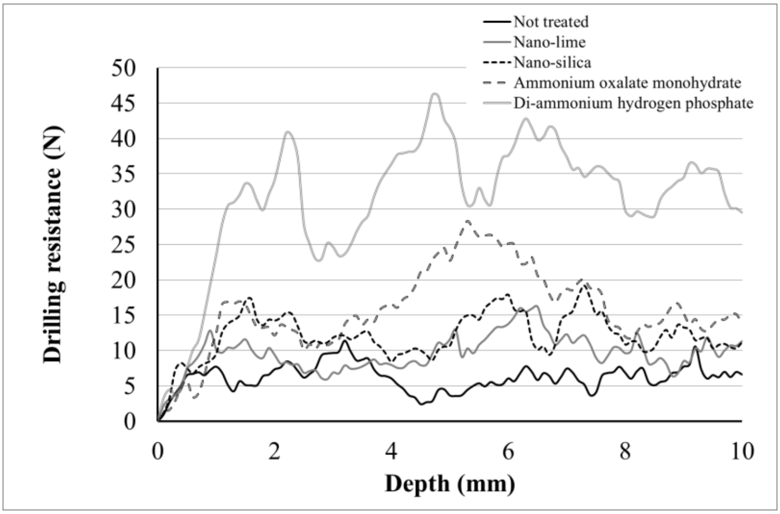


Figure 3. Drilling resistance profiles of area A

In the case of the area treated with di-ammonium hydrogen phosphate, the presence of aggregate of relevant hardness can be evidenced (drilling resistance of about 40N), but on the average the resistance referred to the binder is 15-20N. Considering that the value of the unconsolidated mortar is 5-7 N and taking these values as background, we can infer that the di-ammonium hydrogen phosphate induced a significant consolidation of the mortar (25-30N). Also the ammonium oxalate monohydrate led to a good reconsolidation with values around 15N. Nano-silica shoes slightly lower values (10N) while nano-lime does not cause significant changes in cohesion compared to the untreated area.

As for area B, the drilling resistance indicates a certain reconsolidation of the mortar treated with di-ammonium hydrogen phosphate, while the treatment with nano-silica do not cause any increase in cohesion, rather a decrease. In this case we should take into account the considerable moisture that characterizes the area, a factor that adversely interacts with the nano-silica, and also of the lack of aggregate of the area treated with nano-silica, which lowered the average value of drilling resistance of this area. Also in this case the drilling profiles may provide further indications on the actual situation (Fig.4). In fact, in the non-treated zone and in those treated with di-ammonium hydrogen phosphate the presence of peaks referred to the presence of aggregate is evidenced. These peaks (except one) are not present in the area treated with nano-silica. However, on average, the treatment with di-ammonium hydrogen phosphate appears to have yielded a slight reconsolidation to the mortar.

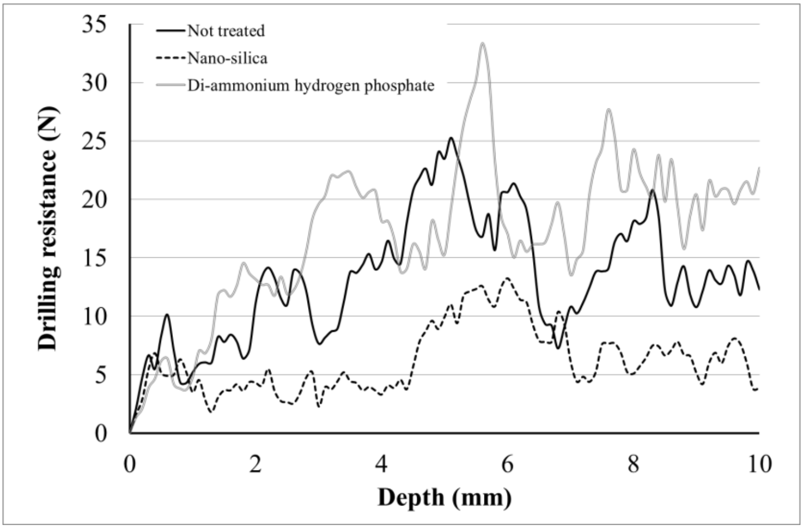


Figure 4. Drilling resistance profiles of area B.

Water absorption test

Also in the interpretation of the water absorption data (Tab. 4) some factors that may have influenced the measurement have to be considered: the surface roughness, the presence of aggregate, the thickness of the plaster. The roughness can cause problems of perfect adherence of the sponge with a consequent smaller absorption surface or a inhomogeneous pressure on the tested area. A larger amount of aggregate decreases the water absorption while a higher thickness of the plaster increases the absorption. Taking into account these problems, with respect to area A, the nano-silica, ammonium oxalate and di-ammonium hydrogen phosphate seem to have caused a significant decrease in water absorption.

Table 4. Water absorption tests for A and B areas.

Area	Treatment	Water absorbed (cc/cm^2s)
A	Not treated	2.875±0.094
	Nano-lime	2.630±0.096
	Nano-silica	1.279±0.054
	Ammonium oxalate monohydrate	1.908±0.092
	di-ammonium hydrogen phosphate	1.326±0.047
B	Not treated	2.329±0.100
	Nano-silica	2.355±0.237
	Di-ammonium hydrogen phosphate	2.057±0.080

As to area B, a less evident variation of the water absorption capacity of the treated areas can be noticed. In particular, only for the area treated with the di-ammonium hydrogen phosphate, a slight decrease of the water absorption is evidenced while the area treated with nano-silica shows an absorption capacity similar to the untreated zone. A possible explanation of this behaviour is the inhomogeneity of the mortar in the B area. In fact the strong presence of aggregate in the non-treated area and in the area treated with di-ammonium hydrogen phosphate could have contributed to the low water absorption capacity of these areas respect to the area treated with nano-silica.

Compositional analyses of the neoformed phases

The phases formed during the reaction between the hydraulic lime, di-ammonium hydrogen phosphate and ammonium oxalate monohydrate are calcium phosphate hydrate (hydroxylapatite) and calcium oxalate di-hydrate (weddellite) respectively. The phases formed from the reaction between the same products and the calcitic magnesian lime are ammonium magnesium phosphate (struvite) and weddellite.

Conclusions

The research concerns the problem of conservation of a remain of the production activity of a kiln of the XIXth century, characterized by a poor cohesion and therefore particularly vulnerable to weather events. This is a common case in archaeological sites and sites of industrial archaeology. For this kind of problems, the protection with appropriate shelters is commonly employed which however often result in considerable drawbacks. In our research we have therefore chosen the way of consolidation with suitable inorganic products compatible with the nature of the material to consolidate and capable to exert their action also in high humidity conditions. The following products have been tested: ammonium phosphate, ammonium oxalate, nano-lime. Together with these products, also nano-silica has been tested as comparison. Taking into account the various parameters that in this *in situ* experimentation may have influenced the measurements (surface roughness, uneven presence of aggregate in the mortar, thickness of the plaster, moisture), the following considerations can be advanced:

- the product that appears to have yielded the best results is the di-ammonium hydrogen phosphate both in term of strengthening effectiveness and water absorption reduction although causing a slight chromatic alteration in one of the two treated zones.
- the treatment with nano-silica appears to be significantly influenced by the presence of moisture. In fact, both the strengthening effectiveness and the decrease of water absorption in the most humid area comparable to the untreated zone. The colour variation falls within the limits of eye detection;
- the treatment with ammonium oxalate average is quite effective both regarding the strengthening and for the reduction of water absorption capacity. The colour variation widely falls within the limits of eye detection;
- the nano-limes, while being compositionally the more compatible materials, do not cause significant changes in the "cohesion" and decrease of water absorption.

We have to recall that these results do not take into account the "test of the time" which is the only one that can guarantee the real effectiveness of the products.

References

[1] Pittaluga D. **"***Cavi d'acciaio su più livelli***"** in Progetto Colore, Ed. Tecniche Nuove, Milano, n. 2 aprile 2012, Periodico nazionale bimestrale, pp.11-12

[2] Pittaluga D. "*Un restauro sostenibile: l'intervento di conservazione e valorizzazione della Fornace Bianchi in località Donegaro a Cogoleto (GE)",* in NAM (Notiziario di Archeologia medievale) n. 1/2012, Ed. All'Insegna del Giglio, Firenze 2012

[3] Matteini, M., Rescic, S., Fratini, F., Botticelli, G. 2011, *Ammonium Phosphates as Consolidating Agents for Carbonatic Stone Materials Used in Architecture and Cultural Heritage: Preliminary Research*, Int. J. Arch. Heritage, 5 (6), pp. 717-736.

[4] Matteini M., Fratini F., Rescic S., 2006: "Durable artificial calcium oxalate for the protection of carbonate based lithotypes", Proceeding of international seminar: *"Theory and Pratice in Conservation. A tribute to Cesare Brandi*", Laboratorio National de Engenharia Civil, Lisbon, 2006, May 4-5, 87-102.

[5] Baglioni, P., Giorgi, R. 2006. Soft and hard nanomaterials for restoration and conservation of Cultural Heritage. Soft Matter, 2, 293-303.

[6] AA.VV., "*Misurare il colore. Spettrofotometria, fotometria e colorimetria. Fisiologia e percezione*", a cura di C. Oleari, Ulrico Hoepli Editore S.p.A., Milano, 1998.

[7] CIE, "*Colorimetry, 3rd edition CIE n° 15.2004*", Vienna, Austria: Commission Internationale de l'Éclairage, 2004.

[8] UNI EN 15886:2010, *Conservation of cultural property - Test methods - Colour measurement of surfaces,* 2010.

[9] Tiano, P., Filareto, C., Ponticelli, S., Ferrari, M. & Valentini, E. 2000. *Drilling force measurement system, a new standardisable methodology to determine the 'superficial hardness' of monument stones: prototype design and validation*. Int. J. Rest. Build. Monuments, 6(2), 115–132.

[10] Fratini, F., Rescic, S.&Tiano, P. 2006. *A new portable system for determining the state of conservation of monumental stones*. Materials and Structures, 39(2), 139–147.

[11] Tiano P., Pardini C., Valutazione in situ dei trattamenti protettivi per il materiale lapideo. Proposta di una nuova semplice metodologia, Arkos, 5 (2004), pp. 30-36.